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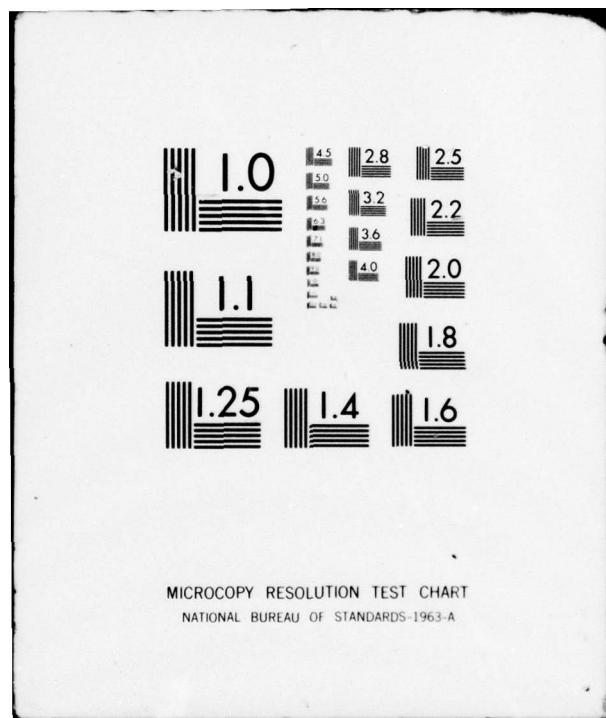
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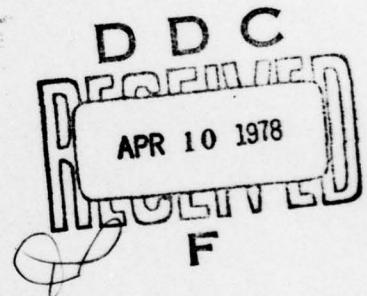
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ABSTRACT

Multicomponent polymers whose structure or composition varies as a function of position in the sample are called gradient polymers. One way to prepare gradient polymers is to permit a guest monomer to diffuse into a host polymer network. The resulting profile of the diffusion gradient is fixed by polymerizing the monomer in situ. In this work, we used 2-chloroethyl acrylate as the monomer and poly(methyl methacrylate) as the polymer matrix. Both gradient polymers and interpenetrating networks were prepared. It was found that the stress-strain behavior of gradient polymers is quite different from that of the interpenetrating networks of comparable composition. The former shows a yield point, and considerably enhanced fracture strain. The latter is essentially rubber in character. Possible mechanisms for the unique properties of gradient polymers are discussed.

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INTRODUCTION

Gradient polymers are multicomponent polymers whose structure or composition is not homogeneous throughout the material, but varies as a function of position (1). In other words, these polymers have gradients in their structures or compositions. In a previous paper (2), we have shown that it is possible to produce such materials by diffusing a guest monomer into a host polymer for a period of time sufficient for the establishment of a diffusion gradient profile. This profile is then "fixed" by polymerization of the monomer in situ. The mechanical behavior of such gradient polymers was found to be quite different from the interpenetrating networks (IPN's) of comparable composition. Of course the latter material allows the monomer to reach a swelling equilibrium in the host polymer, and therefore has no gradient structure.

In our preliminary report (2), we have chosen poly(methyl methacrylate) or PMMA as a host polymer and methyl acrylate as the guest monomer. They were both crosslinked by a divinyl acrylic monomer. However, because of the similarity in the constitutions of these two components, it was not possible to establish the gradient profile through chemical analysis. In this work, we have selected a halogenated acrylic monomer as the second component to be diffused into PMMA. By analyzing the halogen content, it was possible to determine the profiles of the gradient polymers. Stress-strain measurements of the samples were then carried out on these unique materials.

EXPERIMENTAL

Monomers of methyl methacrylate and 2-chloroethyl acrylate (2-C1EA) were purchased from the Polysciences, Inc. They were distilled and subsequently mixed with 1.3% by weight of the crosslinking agent, (ethylene glycol dimethacrylate obtained from the J.T.

Baker Co.), and 1.9% by weight of the photosensitizer (benzoin isobutyl ether supplied by the Stauffer Chemical Co.). PMMA was first prepared by photopolymerization in front of ultraviolet light for 48 hours. Samples were stored in a vacuum oven at 60°C until a constant weight was achieved to remove remaining monomer. The cross-linked PMMA samples were then immersed in the bath of 2-CLEA monomer for various periods of time by monitoring the weight uptake. When the desired amount of monomer has been imbibed into the host polymer, the latter was removed, surface dried and then immediately polymerized by uv radiation. IPN's were prepared in a similar manner, except that after immersion in the monomer bath the sample was stored in a sealed polymerization cell at 60°C for several days prior to polymerization.

The profiles of these gradient polymers were determined by machining off the samples layer by layer. Shavings from each layer were then analyzed for chlorine content by combustion methods (3). The results of these analyses are shown in Figure 1, recalculated in terms of mole percent of 2-CLEA in PMMA.

An Instron Universal Testing Machine Model TM-SM was used to carry out the stress-strain measurements. An environmental chamber, equipped with a Missimers PITC temperature controller, was employed in providing constant temperatures to $\pm 0.5^{\circ}\text{C}$. Samples were of the approximate dimensions of $5.0 \times 0.5 \times 0.1 \text{ cm}^3$. To prevent slippage from the Instron clamps, special aluminum tabs were glued to the ends of the samples.

RESULTS AND DISCUSSION

Stress-strain curves for a series of gradient polymers of 2-chloroethyl acrylate in poly(methyl methacrylate), which are designated

as PMMA/Grad PC1EA, are shown in Figure 2. Quantities in the parentheses indicate the mole percent of the acrylate. Also included are the stress-strain curves of pure PMMA and an interpenetrating network (PMMA/IPN PC1EA). All of these measurements were carried out at 80°C, and at strain rates of 2-3%/sec. First we note that the stress-strain curve of PMMA has a high initial slope (high elastic modulus) and fractures at about 6% strain. Upon introduction of a 5% PC1EA gradient, there is a slight decrease of the initial slope, but a dramatic increase in fracture strain (~65%). In addition, a pronounced yield region is observed around 5% strain. Further increases in PC1EA contents to 12.5 and 29.7% show a continuing decrease in the elastic moduli, but even higher fracture strains were attained (85% and 130% respectively). Both of the latter gradient polymers, however, still exhibit the yielding behavior and are plastic-like in mechanical properties. In contrast the IPN at 29.8% PC1EA content is rubbery and fractures at slightly greater than 100% strain. Apparently the presence of the gradient structure enables the samples to retain the plastic-like properties without sacrificing the enhanced ability to withstand deformation.

In our previous paper (2), we proposed a possible mechanism to interpret the stress-strain behavior of gradient polymers. We perceived the gradient polymer as consisting of infinite number of layers of varying compositions. Upon deformation, the macroscopic strain is the same for the entire sample. Because of the fact that the moduli of the various layers are different due to their differences in composition, those layers with higher moduli must sustain greater stresses (for the same strain). According to Eyring's stress-biased activated rate theory of yielding (4,5), the barrier height for a molecular segment to jump in the forward direction is reduced by the applied stress. As a con-

sequence, the higher modulus layers in the gradient polymer should show greater tendency to yield because of the greater stress biases they have than those with lower moduli. This mechanism will be inoperative for interpenetrating networks because of their uniform composition.

An alternative mechanism for the observed high fracture strain may be the reduction in surface imperfections for the gradient polymers. The surfaces of these materials must be more resistant to fracture because of the relatively high loading of rubbery phases. Thus, under stress they are likely to craze or crack, which would have initiated fracture for the sample as a whole. The validity of either mechanism, however, must await verification.

The effect of the strain rates of PMMA/Grad PC1EA (29.7) and PMMA/IPN PC1EA (29.8) are compared in Figure 3. Increased strain rates are seen to increase the yield stresses as well as stress levels in the plateau regions of the gradient polymers but decrease the fracture strains. For the interpenetrating networks of comparable composition, there is no observable yielding, but the stress levels are increased by higher strain rates. However, there appear to be also decreases in the fracture strains. Again IPN's behave essentially as rubbers, while the gradient polymers exhibit plastic-like properties.

The effect of temperature on the stress-strain properties of PMMA, its gradient polymers with various compositions and an IPN are shown in Figure 4. These experiments were performed at strain rates of the order of 10^{-2} %/sec at 60°C. Comparison with data in Figure 2, which are for the temperature of 80°C shows that the main effects of temperature are to increase the stress levels in the plateau regions at lower temperatures, without significant differences in other aspects.

In conclusion, we find that gradient polymers produced by diffusion polymerization generally show enhanced fracture strain, while retaining their plastic-like properties. This behavior appears to be a consequence of the gradient structure, rather than being due to the compositions alone. Interpenetrating networks with comparable composition do not possess the unique mechanical behavior of the gradient polymers.

ACKNOWLEDGEMENT

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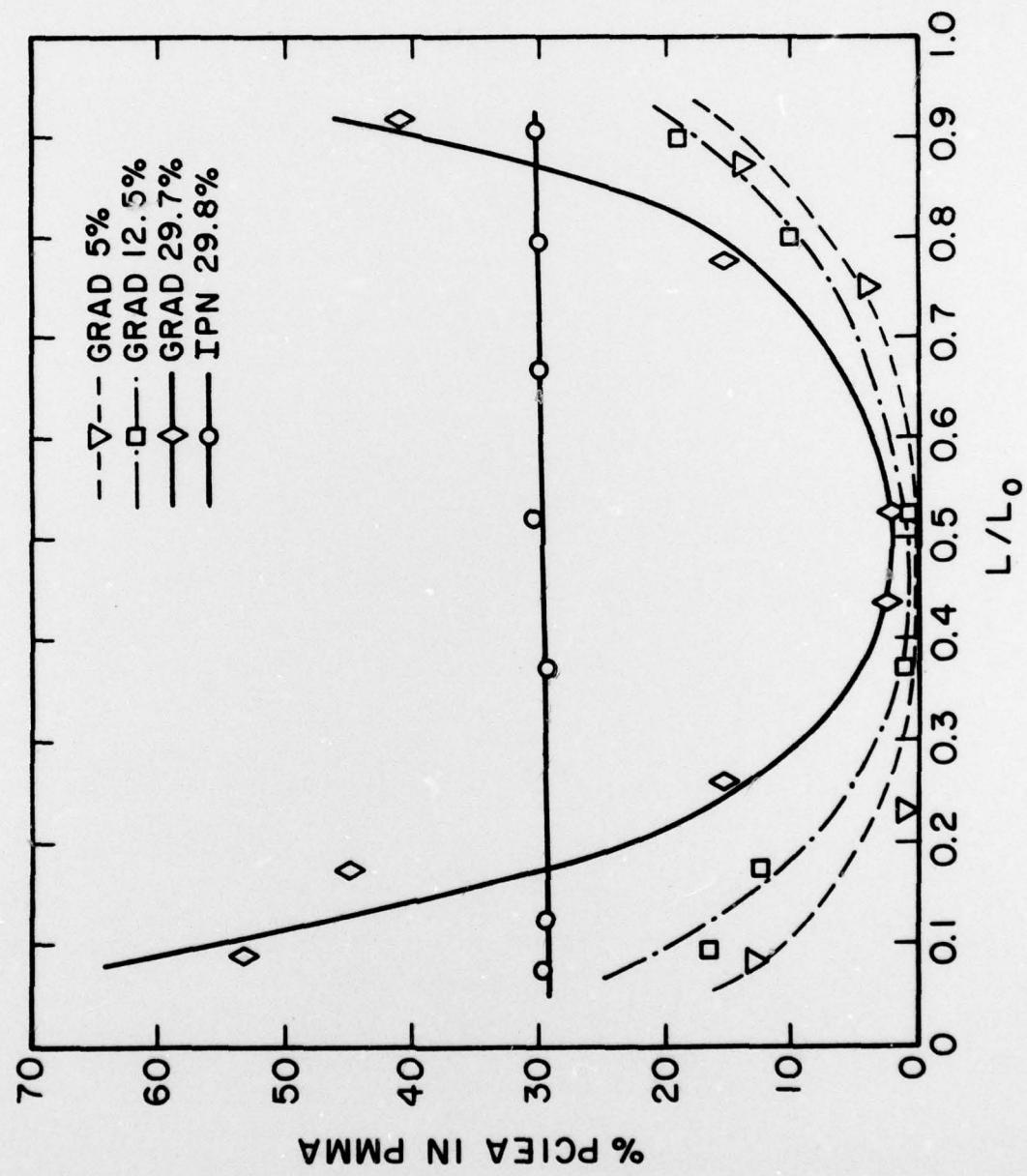
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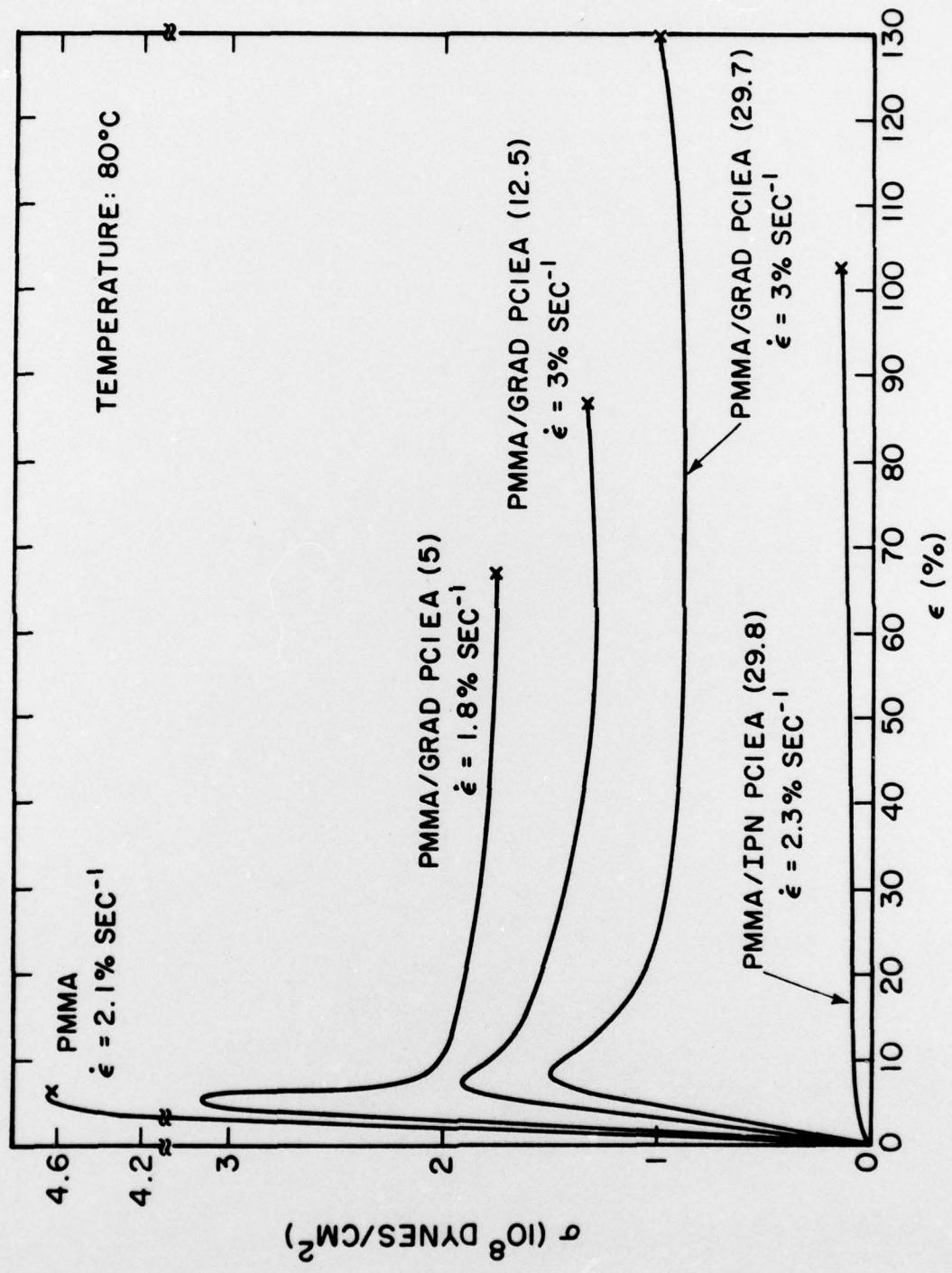
Figure 1: Concentration profiles of poly(2-chloroethyl acrylate) in Poly(methyl methacrylate) along the thickness (L_0) dimension of the samples. GRAD: gradient polymer; IPN: interpenetrating networks.

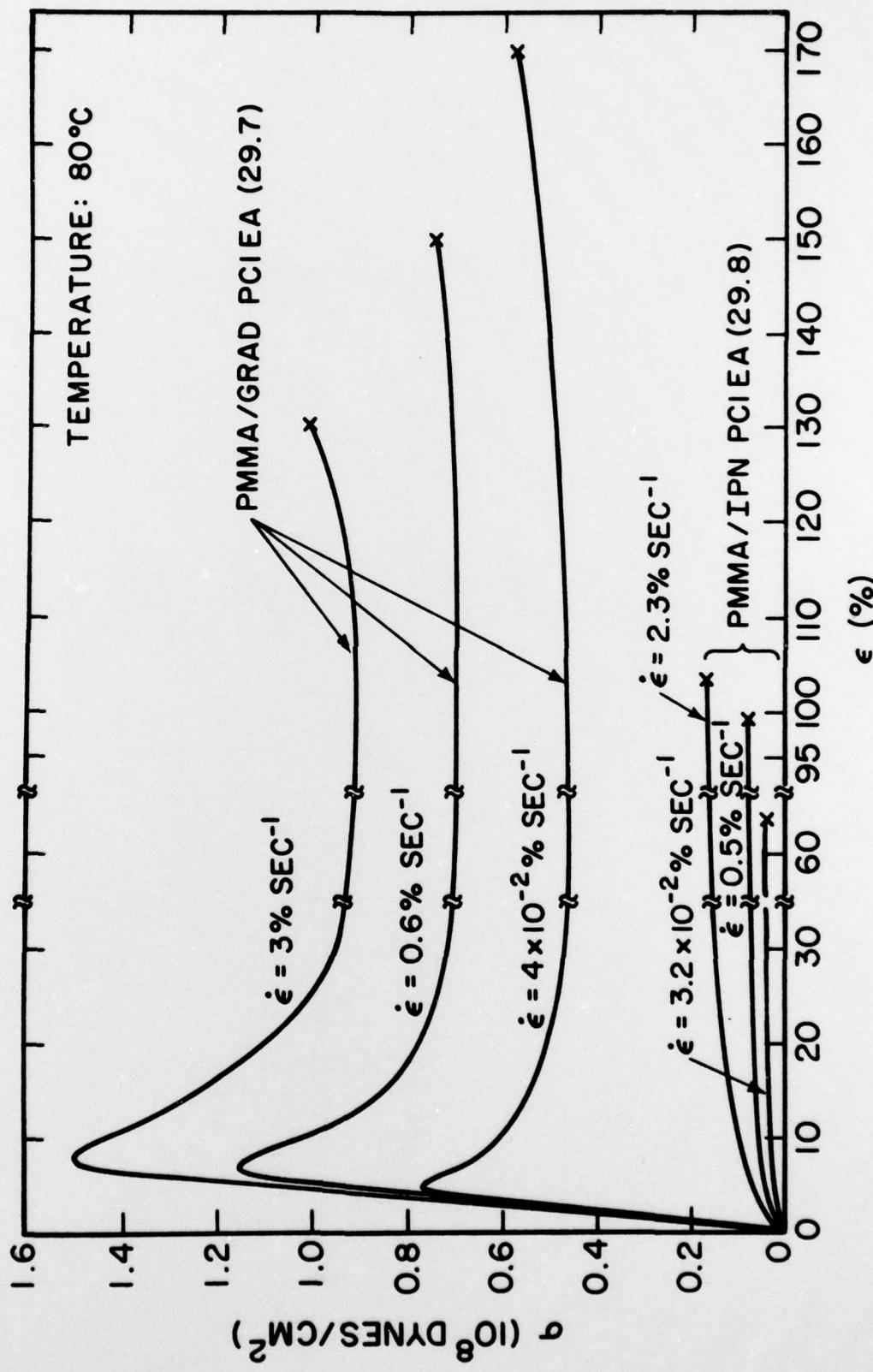
Figure 2: Stress-strain curves of poly(methyl methacrylate) three gradient polymers and one interpenetrating network at comparable strain rates (2-3%/sec) at 80°C.

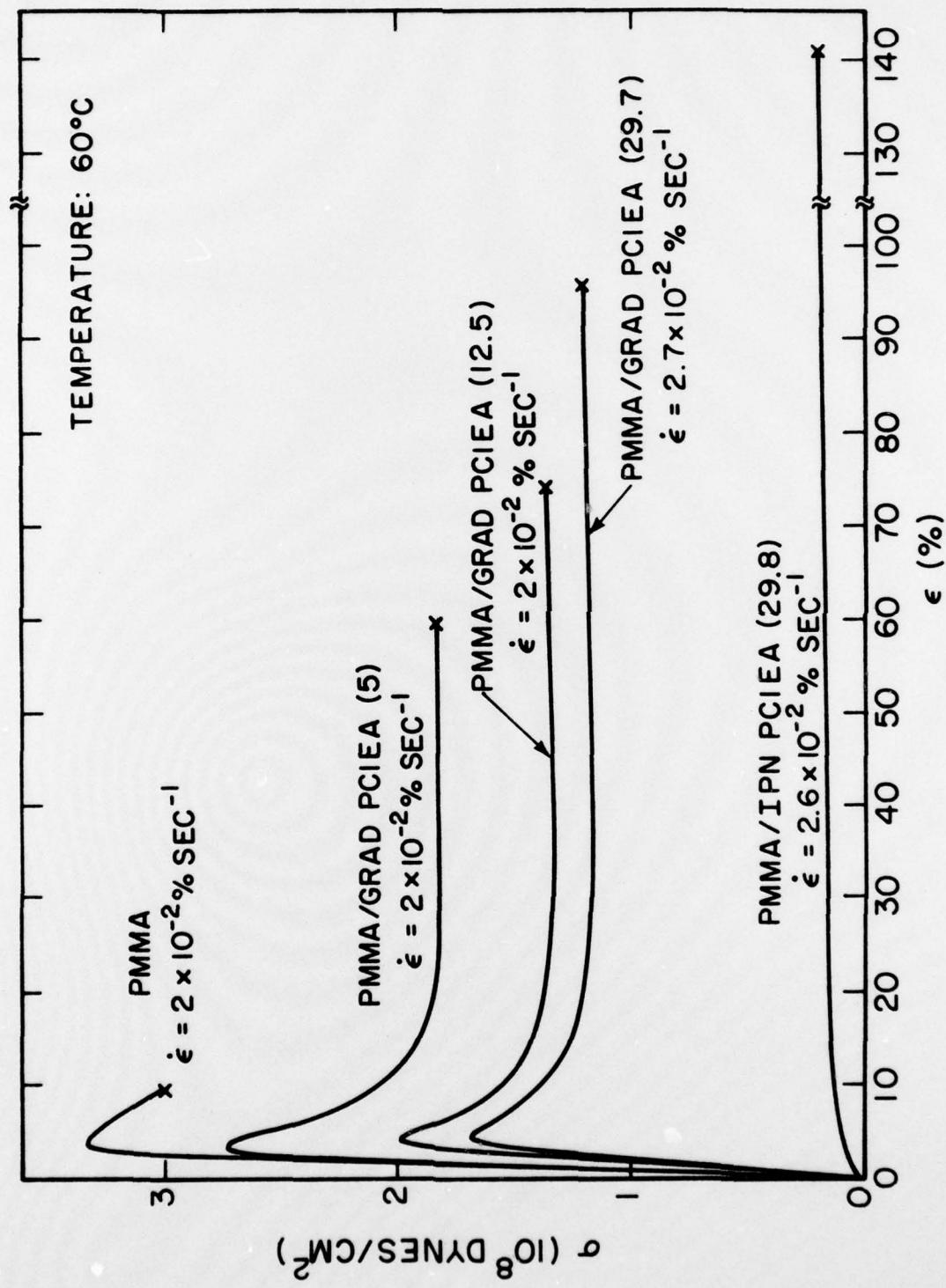
Figure 3: Stress-strain curves of gradient polymer and an interpenetrating network with comparable content of 2-chloroethyl acrylate in poly(methyl methacrylate) at 80°C for a series of strain states.

Figure 4: Stress-strain curves of poly(methyl methacrylate),
three gradient polymers and one interpenetrating network at com-
parable strain rates (2-3%/sec) at 60°C.









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